axial interactions are similar with respect to their type and position in the two different ligands.

One might have expected that dimer formation in NiCu(BAA)$_2$en would have been the result of a Cu(II) axial interaction with an oxygen from the other molecular pair. Indeed, this is common and has even been observed in the mononuclear precursor, Cu(HBAA)$_2$en–O$_2$O$_2$,[2] and in a binuclear Cu(II) triketonate.[2] Judging from the fact that the axial Cu(II)–O distance in Cu(HBAA)$_2$en is 2.27 Å and the Cu(II)–C distance in NiCu(BAA)$_2$en is 3.06 Å, a Cu(II)–O interaction would have afforded the possibility of a much stronger interaction. For some reason, addition of the Ni(II) has lengthened the axial Cu–L distance from 2.27 to 3.06 Å and changed the nature of L from oxygen to carbon (or the π system). Perhaps associated with this change is the fact that the Cu–bridging oxygen bond distance of 1.918 Å is the shortest yet observed for this general class of compounds.[20] While it is not clear whether the axial change has a large effect on the electrochemical properties, it does suggest that the addition of Ni(II) has changed the electronic nature of the axial Cu(II) orbitals and subsequently changed the Lewis acidity of the copper. It is logical to assume that these orbitals are the same ones most strongly affected by the electrode as the molecule diffuses toward the electrode.

If the presumption that the Ni(II) is reduced to Ni(I) in the CV and in the CPE is correct, then the reduction potential for Ni(II) → Ni(I) has been shifted about +0.9 V upon the introduction of Cu(II) into Ni(HBAA)$_2$en. Conceptually a shift of this magnitude is possible, since ligand modifications including changes in remote substituents often cause shifts considerably larger.[16,22-24] Concentrating on just the coordination environment about the Ni(II) may give some clues as to the origin of a potential shift. The bond lengths and angles appear quite normal, but somewhat different from analogous values in Ni(acac)$_2$en.[25] The most significant difference between the Ni(II) environments in Ni(acac)$_2$en and NiCu(BAA)$_2$en seems to be that the average Ni–O bond length in NiCu(BAA)$_2$en is 0.014 Å shorter than in Ni(acac)$_2$en and the average Ni–N distance is 0.024 Å shorter in NiCu(BAA)$_2$en than in Ni(acac)$_2$en. Hence, there appears to be a systematic shortening of the Ni-donor bonds in NiCu(BAA)$_2$en as compared to Ni(acac)$_2$en. The other significant difference is the size of the O–Ni–O angle, which is 79.8° in NiCu(BAA)$_2$en and 82.8° in Ni(acac)$_2$en. Since both Ni atoms are rigorously planar, the smaller angle in NiCu(BAA)$_2$en is compensated by an increase of about 1° in the other three angles.

Another structural parameter of this molecule that distinguishes it somewhat from all the other homo- and heterobinuclear complexes of this class studied to date is the metal–metal distance. The Ni–Cu distance of 2.925 Å is the shortest yet observed by about 0.1 Å. Presumably this is due to the relatively short bonds to the bridging oxygen and the high degree of coplanarity for the metals and donor atoms.

At this point, it is not clear whether or not the structural parameters discussed above have any significant role in establishing the unusual electrochemical properties observed. However, they do draw attention to features that may be important and that form some basis for the design and study of future systems. While we have no satisfactory physical explanation for the observed behavior, phenomenoligically it is similar to the binuclear Cu(II) complexes.[3-5] In many respects, these compounds behave electrochemically as if they had only one electroactive center that is capable of undergoing two-electron redox rather than two centers each capable of one-electron redox. We have not yet observed two separated CV waves for any of the binuclear Cu(II) complexes no matter whether the Cu(II) ions are in equivalent environments (as in symmetric triketonates) or in nonequivalent environments (as in the diamine Schiff bases). The effect of such ligand changes is to perturb the redox center(s) and shift the potential, but they do not bring about two separated Cu(II) → Cu(I) waves. Curiously, the same observation has now been extended to the heterobinuclear complex NiCu(BAA)$_2$en.

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Registry No. NiCu(BAA)$_2$en, 55998-68-0; Ni(HBAA)$_2$en, 55998-67-9; Cu(HBAA)$_2$en, 56550-32-4; Ni(acac)$_2$en, 42948-35-6; NaNO$_3$, 7631-99-4; Na, 7440-23-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, intermolecular distances, hydrogen positions, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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A Bond-Order Function for Metal–Metal Bonds

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For computational purposes multiple bonds are considered as single bonds intensified by screening of the internuclear repulsion. A linear relationship between bond order and screening allows the calculation of multiple-bond properties from single-bond potential energy Morse curves. The scheme is successfully applied for the calculation of bond length and dissociation energy of the homonuclear double, triple, and quadruple bonds of Cr, Mo, W, and Re.

A general relationship between bonds that differ in order only was recently described[1] for bonds between atoms of the p-block elements. The method assumes that bond order derives essentially from changes in the repulsive part of covalent interactions and more specifically from a modification of the internuclear repulsion due to electronic screening. In practice, a single-bond potential energy curve is modified by allowing for reduced internuclear repulsion to produce potential energy curves for bonds of higher order. The modification consists

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Table I. Comparison of Calculated and Observed Bond Parameters

bond	a/a_0	D_e/eV calcd	D_e/eV obsd	ref	r_e/a_0 calcd	r_e/a_0 obsd	ref	k_e/mdyn $Å^{-1} = 1.6a^2D_e$
Re$\overset{1}{-}$Re	0.62		1.34	4		4.93	3	0.82
Re$\overset{2}{-}$Re		2.93			4.65	4.63	2	
Re$\overset{3}{-}$Re		4.78	5.83 ± 1.25		4.35	4.27	2	
Re$\overset{4}{-}$Re		6.60		7	4.25	4.19	6	
Cr$\overset{1}{-}$Cr	0.46		1.03	4		5.043	9	0.35
Cr$\overset{2}{-}$Cr		2.64	1.57	8	4.4			
Cr$\overset{3}{-}$Cr		4.67			3.9			
Cr$\overset{4}{-}$Cr		6.79			3.5	3.49	10	
Mo$\overset{1}{-}$Mo	0.33		2.69	6		5.22	11	0.47
Mo$\overset{2}{-}$Mo		4.24	4.26	8	4.70	4.73	11	
Mo$\overset{3}{-}$Mo		6.15	6.14	7	4.30	4.18	12	
Mo$\overset{4}{-}$Mo		8.03	7.87	7	3.80	4.00	11	
W$\overset{1}{-}$W	0.25		2.43	4		6.085	13	0.24
W$\overset{2}{-}$W		3.76	8.07 ± 2.27		5.40	4.78	14	
W$\overset{3}{-}$W		5.43		12	4.65	4.32	6	
W$\overset{4}{-}$W		7.29			3.80	4.08	6	

of assuming screening factors, $0 < k \leq 1$, which decrease with increasing bond order. A special feature of the method is the constancy of k for any bond of given order; i.e., $k = 0.72$ and 0.41 for any double and triple bonds, respectively. This represents an approximately linear relationship between bond order and screening factor, b and k, according to the equation

$$k = -0.295b + 1.3 \qquad (1)$$

It follows that the maximum integral bond order allowed by the scheme is 4, for which $k = 0.12$ is predicted. It is of interest to see whether this scheme provides a reasonable description of the only bonds known to attain an order of 4, i.e., certain metal–metal bonds.

Method

On the assumption that the relationship between screening factor and bond order found for bonds between p-block atoms also exists for metal–metal bonds, the problem reduces to the formulation of potential energy Morse curves for single metal–metal bonds. Modification of the single-bond curves to allow for screening and to yield potential curves for bonds of higher order is a trivial operation.

The Morse description of a single bond requires specification of the equilibrium bond length, r_e, the bond dissociation energy, D_e, and the quadratic force constant, k_e. One writes

$$V(r) = D_e\{\exp[-2a(r - r_e)] - 2\exp[-a(r - r_e)]\}$$

where $a = 0.9349(k_e/D_e)^{1/2}$ for k_e in units of mdyn $Å^{-1}$ and D_e in eV.

Of the likely atoms for study in this investigation, viz. Cr, Mo, W, and Re, it was only for Re that experimental values of r_e, D_e, and k_e for single bonds were available from the literature. One finds $r_e = 4.93$ a_0 (Bohr radii),[3] $D_e = 1.34$ eV,[4] and $k_e = 0.82$ mdyn $Å^{-1}$;[5] i.e., $a = 0.62$. These values were used to construct a Morse curve for a Re$\overset{1}{-}$Re single bond. Modification of the single-bond Morse curve to allow for screening, according to eq 1, yields d(Re$\overset{2}{-}$Re) = 4.65 a_0, d(Re$\overset{3}{-}$Re) = 4.35 a_0, d(Re$\overset{4}{-}$Re) = 4.25 a_0, D(Re$\overset{2}{-}$Re) = 2.93 eV, D(Re$\overset{3}{-}$Re) = 4.78 eV, and D(Re$\overset{4}{-}$Re) = 6.60 eV. These values compare surprisingly well with experiment. Cotton[2,6] reports bond lengths for the 2-, 3-, and 4-order bonds of 4.63, 4.27, and 4.19 a_0, respectively. The dissociation energy has been measured[7] for the quadruple bond only, $D = 5.83 \pm 1.25$ eV.

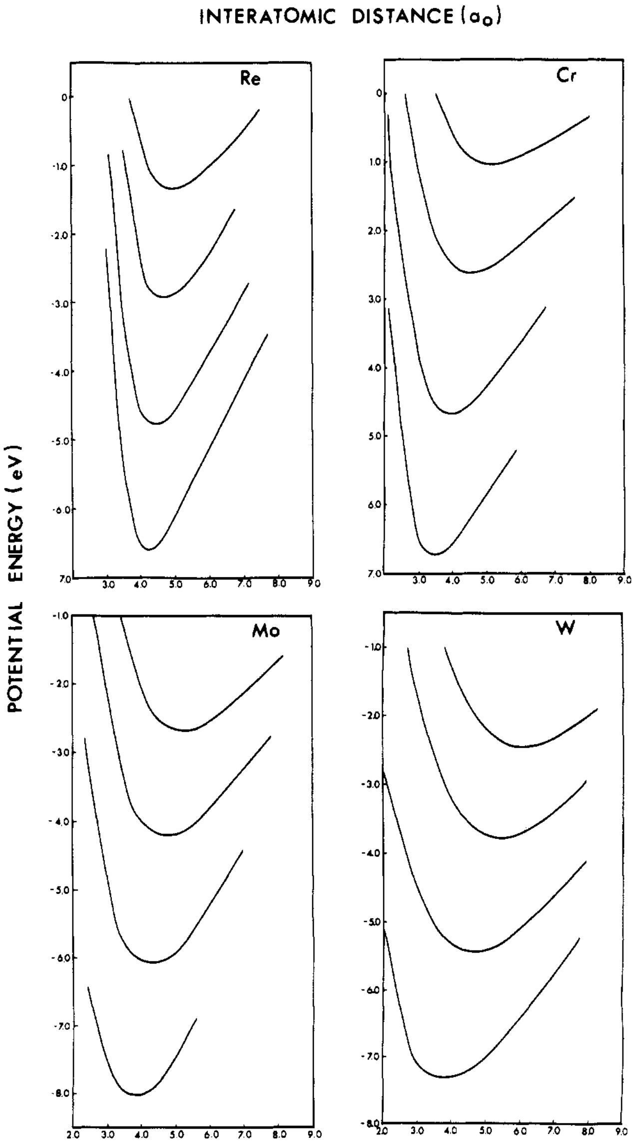

Figure 1.

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This agreement for Re–Re bonds demonstrates the applicability of the method to bonds between d-block atoms, and even though reliable values of k_e for the group 6B metals are not at hand, these can easily be generated by variation of the constant a to ensure the best fit between calculated and observed values of r_e and D_e for the higher order bonds.

Results

The Morse constants, a, were varied in each case within limits established by analogy with approximate values of the corresponding double-bond force constants estimated from diatomic molecular spectra. This produced reasonable values of multiple-bond lengths and dissociation energies, in fair agreement with available experimental values. The results for all calculations are summarized in Table I and illustrated graphically in Figure 1.

The major defect of the comparison is the dearth of reliable experimental values for the quantities of interest. Clearly, erroneous definition of the single bond produces poor predictions of the properties of the higher order bonds. Evaluation of the agreement should hence not be too strict. In view of this, the agreement between calculated and observed bond properties is excellent, especially for the $\mathrm{Re}\overset{n}{-}\mathrm{Re}$ and $\mathrm{Mo}\overset{n}{-}\mathrm{Mo}$ bonds.

Discussion

A common problem in the field of metal–metal bonding is the assignment of exact bond orders. In many cases bond orders actually appear to be fractional rather than integral. This is not always easy to rationalize in terms of the established models of multiple bonding. In terms of the screening mechanism proposed here, it presents no problem. In fact, bonds of exactly integral order would be the exception rather than the rule insofar as eq 1 relates bond order to electron density in the region between atomic cores. This electron density must be sensitive to the nature of any ligands attached to the bonded atoms. In a variety of compounds, one therefore expects metal–metal bond orders spanning the whole region from 1 to 4 instead of well-defined integral bond orders only. In many ways this agrees with experience.

In view of recent criticism[10] of Cotton's formulation of quadruple bonds, the present results have additional significance. It provides independent evidence of a heuristic nature to support Cotton's model. Starting from eq 1, together with characteristic single-bond properties, one predicts the properties of multiple bonds, in good agreement with the most reliable experimental values. In the sense of the bond order concept as commonly applied to bonds between p-block atoms, bond order 4 is therefore seen to occur with the homonuclear bonds of Cr, Mo, W, and Re.

The present approach does not stipulate the electronic distribution of the higher order bonding electrons, but in order to satisfy the requirements of the Pauli principle for the internuclear region, molecular orbitals of the type proposed by Cotton would clearly be required.

Future work will be directed toward the characterization of bond orders for the large number of intermediate-type bonds that occur in metal clusters.

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Mechanistic Difference of the Iron(III) Ion Complexation in Different Solvents

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The activation volumes (ΔV^*) for the complexation of the iron(III) ion with acetohydroxamic acid, 4-isopropyltropolone, and thiocyanate ion in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO) were determined by a high-pressure stopped-flow technique. Values of ΔV^* for the formation of the (acetohydroxamato)iron(III) and (isopropyltropolonato)iron(III) complexes are -0.8 ± 0.2 and 5.0 ± 0.4 cm^3 mol^{-1}, respectively, in DMF and 3.0 ± 0.3 and 10.9 ± 1.7 cm^3 mol^{-1} in Me_2SO, respectively. For the formation and dissociation of the 1:1 (isothiocyanato)iron(III) complex in Me_2SO, the ΔV^* values are 3.3 ± 0.6 and -8.5 ± 1.4 cm^3 mol^{-1}, respectively. The change in the sign of ΔV^* is interpreted on the basis of relative bulkiness of both the entering ligand and the coordinated solvent molecule.

Introduction

The mechanism of the complexation of the iron(III) ion and the solvent exchange on the iron(III) ion has been studied in acidic aqueous solution at high pressures.[1-3] It has been concluded from the sign of the activation volumes (ΔV^*) that the hexaaquairon(III) ion reacts through an associative interchange (I_a) mechanism but the pentaaquahydroxoiron(III) ion via a dissociative interchange (I_d) mechanism. Recently we have concluded that all the formation and dissociation of the 1:1 nickel(II) complex and the solvent exchange on the nickel(II) ion in various solvents can be accommodated within the framework of a similar I_d mechanism.[4]

Recently, interesting data on activation volumes for the nonaqueous solvent exchange on the Fe(III) ion were reported by Merbach et al.[5] Values of ΔV^* for the solvent exchange on the Fe(III) ion in Me_2SO (-3.1 ± 0.3 cm^3 mol^{-1}) and in DMF (-0.9 ± 0.2 cm^3 mol^{-1}) are less negative in comparison

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